J Therm Anal Calorim (2013) 111:1019–1024
DOI 10.1007/s10973-012-2506-0

The effect of carbon nanotubes on epoxy matrix nanocomposites

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Received: 11 October 2011 / Accepted: 18 May 2012 / Published online: 3 July 2012

Abstract The paper concerns thermal properties of epoxy/nanotubes composites for aircraft application. In this work, influence of carbon nanotubes on thermal stability, thermal conductivity, and crosslinking density of epoxy matrix was determined. Three kinds of nanotubes were used: non-modified with 1- and 1.5-μm length, and 1-μm length modified with amino groups. Scanning electron microscopy observations were done for examining dispersion of nanotubes in the epoxy matrix. Glass transition temperature (T_g) was readout from differential scanning calorimetry. From dynamic mechanical analysis, crosslinking density was calculated for epoxy and its composites. Also, thermogravimetric analysis was done to determine influence of nanotubes addition on thermal stability and decomposition process of composites. Activation energy was calculated from TGA curves by Flynn–Wall–Ozawa method. Thermal diffusivity was also measured. SEM images proved the uniform dispersion of carbon nanotubes without any agglomerates. It was found that nanotubes modified with amino groups lead to the increase of epoxy matrix crosslinking density. The significant increase in T_g was also observed. On the other hand, addition of carbon nanotubes leads to the decrease of thermal stability of polymer due to the increase of thermal diffusivity.

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Keywords Nanocomposites · Carbon nanotubes · Polymer matrix composites · Thermal properties · Activation energy · Crosslinking density

Introduction

Carbon nanotubes, CNTs, owing to their attractive mechanical, thermal, and electrical properties have found a wide range of applications, including nanomodifier of polymer composites. Main challenge in manufacturing nanocomposites is the uniform dispersion of CNTs in polymer matrix, often realized via calendering and/or sonification [1, 2]. To improve the adhesion of CNTs to the polymer matrix, their surface is frequently functionalized by amino or carboxyl groups.

Epoxy resin is often used as a matrix of fiber-reinforced composites for advanced applications. Addition of CNTs results in a significant improvement of epoxy resin, in particular in an increase of the electrical conductivity by a few orders of magnitude. This is accompanied by an increase of thermal conductivity [3, 4]. On the other hand, some results indicate that the addition of carbon nanotubes may deteriorate thermal stability of the epoxy matrix [5, 6]. It has been also reported that modification with nanotubes changes glass transition temperature, T_g [7], which in the case of the CNTs functionalised with amino groups considerably increases [8]. In this context, the aim of this work was to investigate the thermal properties of epoxy-nanotube composites with CNTs of different lengths and subjected to different surface functionalization. To this end, several thermal characteristics have been measured for epoxy/CNTs nanocomposites. These characteristics and the results of the microstructure investigations are discussed in terms of the effect of CNTs on the epoxy matrix of nanocomposites.

Experimental

Materials

The multi-wall carbon nanotubes, with oxides content of 5 wt%, were supplied by Nanocyl Inc. (Belgium). CNTs with two lengths, 1.5 and 1.0 μm were employed. Part of the 1 μm CNTs were functionalized with amino groups. Average tube diameter in each case was equal to 9.5 nm. The CNTs were dispersed in the epoxy resin EPON 862 (diglycidyl ether of bisphenol-F) supplied by Hexion. EPIKURE W (aromatic di-amine) was used as the curing agent. The Stoichiometric ratio of EPON 862 to EPICURE W was 100:26.4 by weight.

Samples of nanocomposites were prepared with nanotubes weight fraction varying from 1 to 5 %. The resin, curing agent, and CNTs were first mixed manually and subsequently with three-roll mill. First, the mixture was stirred under a gap of 50 μm and 100 rpm. For second stirring, 20-μm gap was used. Finally, the mixture was stirred three times with 10-μm gap. After stirring, the mixture was placed into a mold and was degassed and cured for 6 h at 130 °C.

Measurements

Microstructure observations were performed using Scanning Electron Microscope HITACHI S5500. Differential scanning calorimetry was carried out using DSC Q1000 (TA). Thermal diffusivity was measured using LFA 447 NanoFlash (NETZSCH). Thermal properties were also examined using thermogravimetric analyzer TGA Q500 (TA) in the temperature ranging from 25 to 600 °C under nitrogen. Heating rate was 5 °C per minute. Activation energy was calculated from TG curves for four heating rates: 5, 10, 15, and 20 °C min^{-1}. Dynamic mechanical analysis was made using DMA 983 (TA) in the temperature range of RT to 220 °C. Rate of heating was 2 °C min^{-1}. Crosslinking density was determined from dynamic mechanical analysis by calculating the average molar mass of elastically effective chains between crosslinks (M_c) by Eq. 1 [9, 10]:

$$E \approx \frac{3\rho RT}{\overline{M_c}} \tag{1}$$

where E is the elastic modulus in 20 °C above T_c determined from DMA curves as it is shown in Fig. 3, T_c is the extrapolated temperature when E slightly decreases [K], ρ is the polymer density, R is the gas constant, and T is the absolute temperature.

Results and discussion

Microstructure of the samples was investigated via SEM observations of the brittle fracture surfaces obtained by impact loading of the samples cooled to the temperature of liquid nitrogen. Representative images obtained in this way are presented in Fig. 1. They provide evidence of the uniform dispersion of carbon nanotubes in the epoxy matrix independently of their length and surface modification. The SEM images also proved that calendering employed in this work leads to the even distribution of CNTs into epoxy matrix.

DSC curves for epoxy resin and the composites are shown in Fig. 2 and the values of glass transition temperature calculated from the curves are listed in Table 1.

The results shown in Table 1 demonstrate that the addition of carbon nanotubes with amino groups leads to the increase of the glass transition temperature. This can be caused by the reaction between amino groups located on the CNTs' surface and epoxide groups of the epoxy resin although the amount of functional groups on the nanotubes surface is only 0.5 % by weight. Such small amount of amino groups should not have influence on the crosslinking density, especially when it is compared to curing agent amount (20 wt%). The effect of the CNTs on the matrix is caused by the high specific surface area of CNTs per the unit volume of a composite, S_V. The value of S_V parameter was estimated from purely geometrical considerations. Surface of an individual carbon nanotube is given by Eq. 2:

$$S = 2\left(\pi rL + \pi r^2\right) \tag{2}$$

where L is the length of the tube and r is its radius ($r \ll L$).

A given weight fraction of the nanotubes was converted into its volume fraction, V_V, by means of Eq. 3:

$$V_V = \frac{V_{CNT}}{V_{CNT} + V_{polimer}} = 0.88\% \tag{3}$$

Volume of a single tube can be approximated as $V \approx \pi r^2 L$.

The number of CNTs (for 1 wt% of CNT) in the unit volume (N_v) is given by Eq. 4:

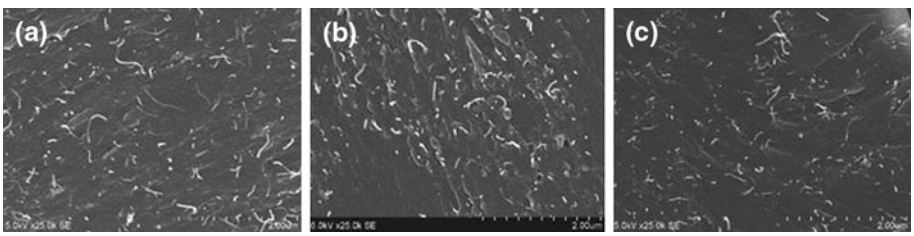

Fig. 1 SEM images of the composites with different kind of nanotubes: **a** 1.5-μm non-modified, **b** 1-μm non-modified, **c** 1-μm nanotubes modified with amino groups

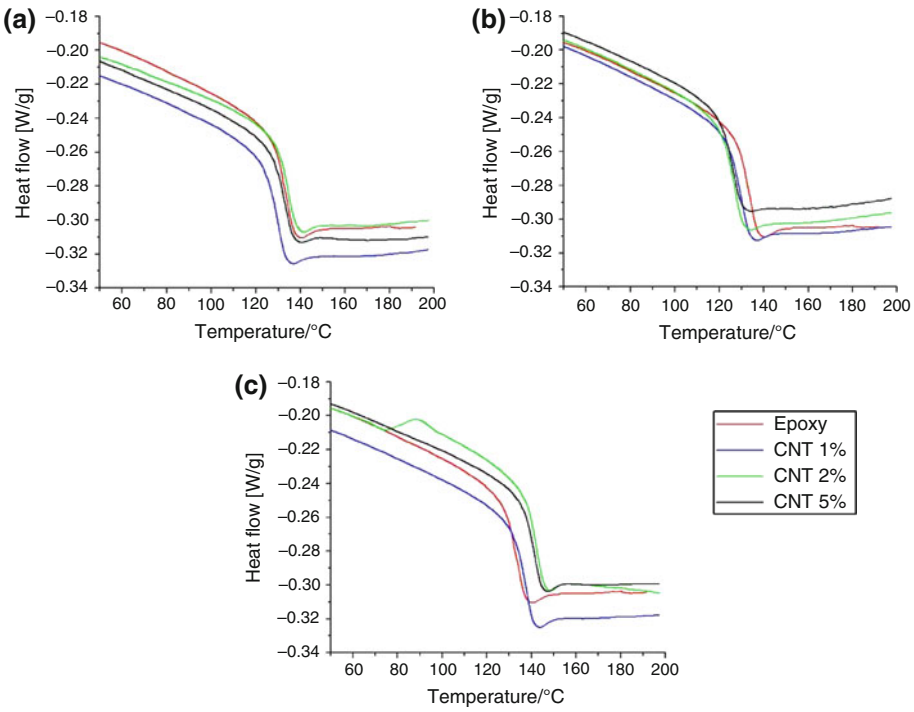

Fig. 2 DSC curves of composites with **a** 1.5-μm non-modified nanotubes, **b** 1-μm non-modified nanotubes, **c** 1-μm nanotubes modified with amino groups

Table 1 Glass transition temperature of epoxy and epoxy-nanotube composites with different amount and different kind of nanotubes

Sample	Epoxy	Composites with non-modified nanotubes l–1.5 μm			Composites with non-modified nanotubes l–1 μm			Composites with nanotubes with amino groups l–1 μm		
		1 %	2 %	5 %	1 %	2 %	5 %	1 %	2 %	5 %
T_g (°C)	133 ± 0.5	129 ± 0.5	134 ± 0.5	132 ± 0.5	130 ± 0.5	127 ± 0.5	126 ± 0.5	137 ± 0.5	142 ± 0.5	141 ± 0.5

$$N_V = \frac{V_V}{V} = \frac{V_V}{\pi r^2 L} \tag{4}$$

The specific surface area of CNTs per unit volume of composite is equal to 1.853 [1/μm], which was calculated from Eq. 5, where $r = 0.0095$ μm:

$$S_V = N_V S = \frac{V_V(2\pi rL)}{(\pi r^2 L)} = \frac{2V_V}{r} \tag{5}$$

High surface area of carbon nanotubes is the most probable reason of significant changes of the nano-composites mechanical as well as thermal properties due to the interaction between carbon nanotubes and polymer macromolecules. When CNTs' surface is modified with reactive amino groups, the macromolecules lose their flexibility in the area around tubes due to the chemical reaction between $–NH_2$ and oxarine ring of epoxy resin during curing reactions. Equations 2–5 consider ideal cylinders with length and diameter equal to the average data furnished by the CNT producer.

The average molar mass of the elastically effective chains between crosslinks (M_c) was determined from DMA studies to analyze the influence of carbon nanotubes on the crosslinking density. It is known from the literature that crosslinking density can be obtained by DMA by calculating M_c [11]. Equation 1 is poor the approximation for the composite materials. Although this is a rough method for crosslinking density determination, it is the only one available on a practical level. From DMA curves, storage modulus was obtained in the way

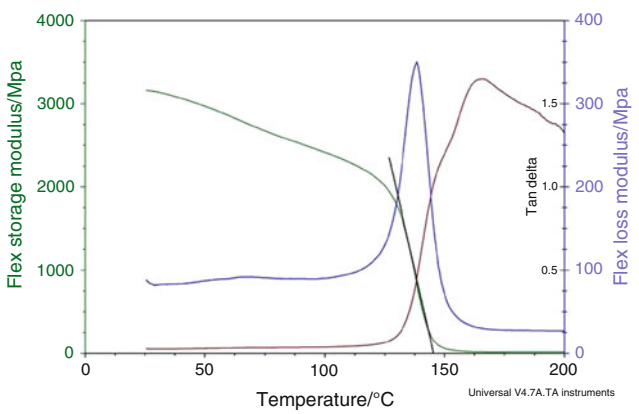

Fig. 3 DMA curve of epoxy resin with determined storage modulus

Table 2 Average molar mass of elastically effective chains of epoxy resin and epoxy-nanotubes composites with different amount and kind of nanotubes

Sample	Weight% of CNTs	ρ/ g cm^{-3}	E'/ MPa	M_c/ g mol^{-1}
Epoxy	0	1.1972	19.02	685
Composites with non-modified nanotubes l–1.5 μm	0.1	1.1994	18.22	713
	1.0	1.1977	24.90	517
	2.0	1.1996	36.60	358
Composites with non-modified nanotubes l–1 μm	0.1	1.1959	15.32	833
	1.0	1.1939	24.88	517
	2.0	1.1939	31.63	403
Composites with nanotubes with amino groups l–1 μm	0.1	1.1925	23.97	556
	1.0	1.1977	36.67	360
	2.0	1.1973	40.62	329

shown in Fig. 3, and by Eq. 1 the average molar mass between crosslinks was calculated. The results are listed in Table 2.

The average molar mass of chains between crosslinks (M_c) significantly decreases after the addition of carbon nanotubes modified with amino groups, which means that the crosslinking density increases due to the reaction between reactive amino groups and oxarine ring of epoxy resin. With the addition of non-modified carbon nanotubes, the crosslinking density decreases for the small amount of CNTs. However, at higher nanotube content, it increases. For higher nanotube content, an obtained significant increase of specific surface of nanotubes affects the macromolecules and prevents the free movement of polymer chains. The free volumes between macromolecules are occupied by carbon nanotubes; therefore, chains are much more squeezed and crosslinking density increases.

Thermogravimetric curves of nanocomposites are shown in Fig. 4. These curves differ in the decomposition rate and mass residue. The temperature of 5 % of mass loss was chosen to define the matrix decomposition temperature. The values of such defined decomposition temperature,

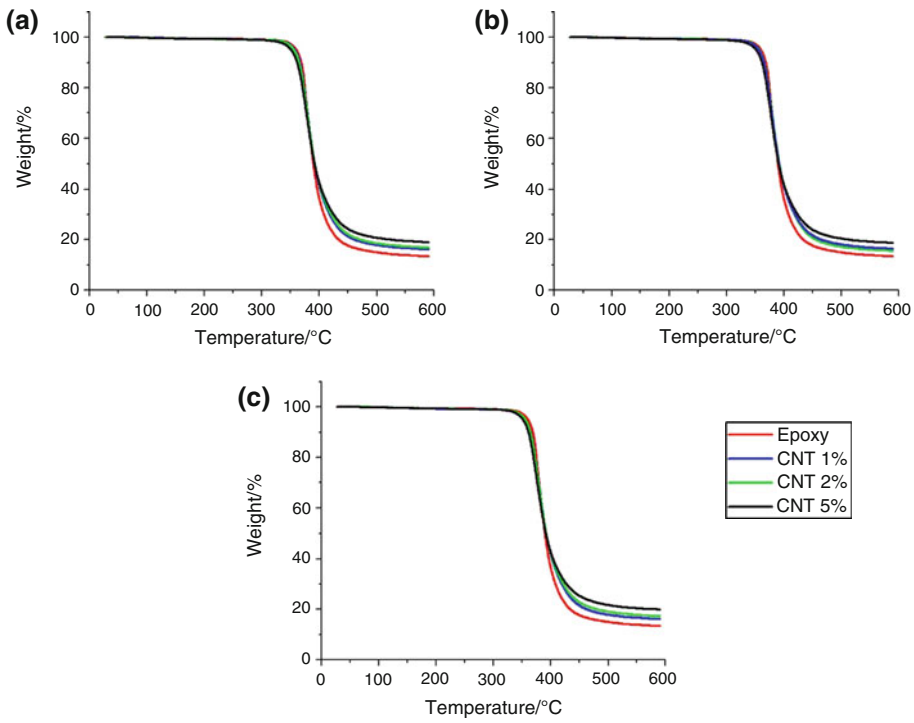

Fig. 4 Thermogravimetric curves of composites with **a** 1.5-μm non-modified nanotubes, **b** 1-μm non-modified nanotubes, **c** 1-μm nanotubes modified with amino groups

Table 3 Temperature of 5 mass% loss of epoxy and epoxy-nanotube composites with different amount and kind of nanotubes

Sample	Epoxy	Composites with non-modified nanotubes l–1.5 μm			Composites with non-modified nanotubes l–1 μm			Composites with nanotubes with amino groups l–1 μm		
		1 wt%	2 wt%	5 wt%	1 wt%	2 wt%	5 wt%	1 wt%	2 wt%	5 wt%
Temperature of 5 mass% loss (°C)	360 ± 0.5	358 ± 0.5	356 ± 0.5	351 ± 0.5	357 ± 0.5	357 ± 0.5	352 ± 0.5	355 ± 0.5	355 ± 0.5	350 ± 0.5

calculated from the thermogravimetric curves, are listed in Table 3.

For all studied composites, the decomposition temperature decreases with the increase of the carbon nanotubes' weight fraction. This results in a decrease in the thermal stability of polymers as a side effect of nanotube addition. Similar results were reported in [5, 6, 12, 13]. The nanotubes' length and modification with 13 amino groups have no significant influence on the decomposition temperature. The decrease in the temperature of 5 % weight loss is caused by the increase of thermal conductivity of polymer as an effect of CNTs addition. Carbon nanotubes increase the heat diffusion which results in faster degradation of polymer. The influence of CNTs' weight fraction on thermal diffusivity of composites is shown in Fig. 7.

The kinetics of the decomposition processes have been characterized by the activation energy calculated from TGA curves by the method proposed by Flynn–Wall–Ozawa, FWO. The Flynn–Wall–Ozawa model provides the following equation:

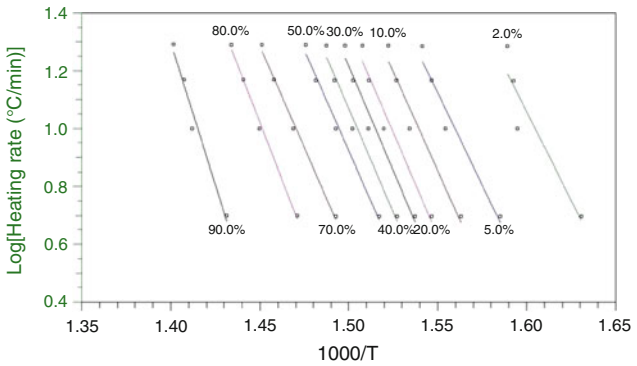

Fig. 5 The dependence of logarithm of heating rate versus reciprocal absolute temperature for the FWO method at indicated conversions of the epoxy resin

$$\log(q) = \log\left[\frac{AE_a}{g(a)R}\right] - 2.315 - \frac{0.457E_a}{RT_p} \quad (6)$$

where $g(a)$ is a function of degree of cure α, q is the heating rate, and T_p is the peak exothermal temperature [14].

In this case, an ASTM Standard E164 was used. For this purpose, several TGA curves were collected at different heating rates. In the case of reported studies, the rates were varied from 5 to 20 °C min^{-1}.

The logarithm of the heating rate was plotted versus $1/T$ for a few degrees of the conversion of epoxy resin as shown in Fig. 5. The activation energy was calculated by means of a TA Instrument software as $E_a = -$ slope $\times$ $R/0.457$ (where R is gas constant) [15]. The results of calculations are shown in Fig 5.

For all investigated nanocomposites, the activation energy is lower for all conversion degrees in comparison to neat epoxy resin. It means that addition of CNTs increases the material's degradation efficiency. CNTs exhibit high thermal conductivity; they help to transport heat in composites, which reduces the activation energy. However, further investigations to explain the mechanism of the degradation will be carried out (Fig. 6).

The studies shown in Fig. 7 confirmed the increase of thermal diffusivity of nanocomposites in comparison to the epoxy matrix. Moreover, thermal diffusivity depends on the CNTs' weight fraction and length.

Thermal diffusivity increases with the increase of carbon nanotubes' weight fraction because nanotubes exhibit very good thermal conductivity. Addition of 5 wt% of CNTs to the epoxy resin almost doubles the thermal diffusivity. Higher thermal diffusivity was also obtained for composites with longer nanotubes. Longer carbon nanotubes create percolated network much easier than shorter one. The same tendency was reported in the literature [16].

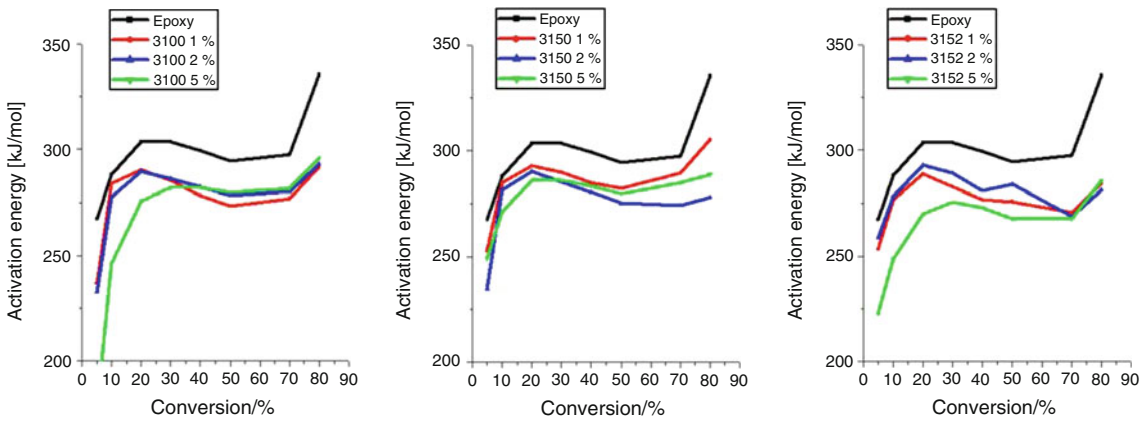

Fig. 6 Activation energy of the composites with **a** 1.5-μm non-modified nanotubes, **b** 1-μm non-modified nanotubes, **c** 1-μm nanotubes modified with amino groups

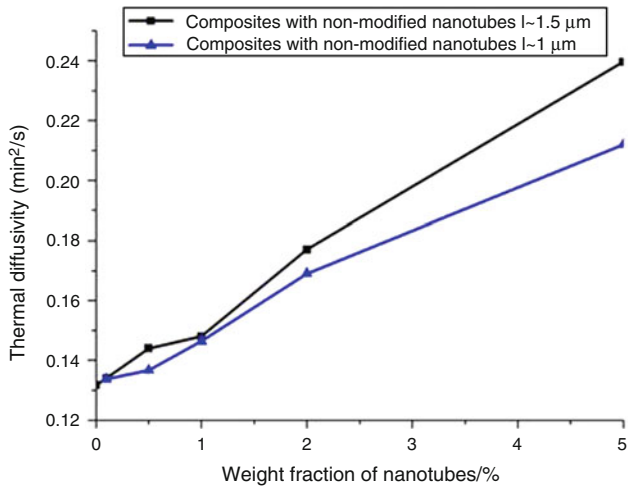

Fig. 7 Thermal diffusivity of composites with different kind of nanotubes

Conclusions

It was found that the addition of carbon nanotubes to the epoxy matrix affects the thermal properties of nanocomposites. Moreover, the reported influence depends on the carbon nanotubes' surface modification and also on their length.

The obtained results proved that the addition of carbon nanotubes with amino groups leads to the increase of the glass transition temperature as well as crosslinking density as an effect of the reaction between amino and hydroxyl reactive groups. Although the weight fraction of amino groups on the carbon nanotubes surface seems to be negligible in comparison to the weight fraction of curing agent, the influence is recordable due to the high specific surface area of nanotubes.

SEM observations confirmed that calendering leads to the good and uniform dispersion of carbon nanotubes in the epoxy matrix independently on their length and surface modification.

The results shown in this paper also confirmed that the addition of carbon nanotubes leads to the decrease in thermal stability of epoxy matrix as an effect of thermal conductivity increase.

Thermal diffusivity of nanocomposites increases with the increase of carbon nanotubes' weight fraction and their length. This also leads to the lower energy needed for the decomposition of nanocomposites.

Acknowledgements This work has been supported by the European Union in the framework of European Social Fund through the Warsaw University of Technology Development Programme.

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